DT06-05.7 U
5/5/99

TestAmerica, Inc.

Dayton Division

Standard Operating Procedure

Analyte or Suite: Volatile Organic Compounds

Methodology: Purge & Trap Gas Chromatography/Mass Spec.

Reference: SW-846 Method 8260A; September 1994

Revision: 7 Date revised: May 5, 1999

File Name: /usr3/sops/1999/SW-8260A

Approvals:

B. Chris Weathington
Division Manager

James A. Davis
Quality Assurance Coordinator

Table of Contents

1. INTRODUCTION AND SCOPE

1.1. This method is used for the determination of volatile organic compounds in a variety of liquid and solid waste matrices. Table 1 lists the compounds that may be determined by this method and the reporting limit (RL) for each compound.

1.2. This method is based upon a purge and trap, gas chromatographic/mass spectrometric (GC-MS) procedure. This method is restricted to use by, or under the supervision of, analysts certified in the use of purge and trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

Table 1. Reporting Limits of Analytes Amenable by Method 8260

QC Use	Analyte	Aqueous RL (ug/L)	Non-Aqueous RL (ug/Kg)
K	Benzene	5.0	5.0
	Bromobenzene	5.0	5.0
	Bromochloromethane	5.0	5.0
	Bromodichloromethane	5.0	5.0
T S	4-Bromofluorobenzene	----	----
P	Bromoform	5.0	5.0
	Bromomethane	10.	10.
	n-Butylbenzene	5.0	5.0
	sec-Butylbenzene	5.0	5.0
	tert-Butylbenzene	5.0	5.0
	Carbon tetrachloride	5.0	5.0
P K	Chlorobenzene	5.0	5.0
I	Chlorobenzene-d5	----	----
	Chloroethane	10.	10.
C	Chloroform	5.0	5.0
P	Chloromethane	10.	10.
	2-Chlorotoluene	5.0	5.0
	Dibromochloromethane	5.0	5.0
	4-Chlorotoluene	5.0	5.0
	1,2-Dibromo-3-chloropropane	5.0	5.0
	1,2-Dibromoethane	5.0	5.0
	Dibromomethane	5.0	5.0
	1,2-Dichlorobenzene	5.0	5.0
	1,3-Dichlorobenzene	5.0	5.0
	1,4-Dichlorobenzene	5.0	5.0
I	1,4-Dichlorobenzene-d4	----	----
	Dichlorodifluoromethane	5.0	5.0

Table 1 continued.

QC Use	Analyte	Aqueous RL (ug/L)	Non-Aqueous RL (ug/Kg)
P	1,1-Dichloroethane	5.0	5.0
	1,2-Dichloroethane	5.0	5.0
S	1,2-Dichloroethane-d4	----	----
C K	1,1-Dichloroethene	5.0	5.0
	cis-1,2-Dichloroethene	5.0	5.0
	trans-1,2-Dichloroethene	5.0	5.0
C	1,2-Dichloropropane	5.0	5.0
	1,3-Dichloropropane	5.0	5.0
	2,2-Dichloropropane	5.0	5.0
	1,1-Dichloropropene	5.0	5.0
I	Fluorobenzene	----	----
C	Ethylbenzene	5.0	5.0
	Hexane	10.0	10.0
	Hexachlorobutadiene	5.0	5.0
	Isopropylbenzene	5.0	5.0
	p-Isopropyltoluene	5.0	5.0
	Methylene chloride	5.0	5.0
	Naphthalene	5.0	5.0
	n-Propylbenzene	5.0	5.0
	Styrene	5.0	5.0
	1,1,1,2-Tetrachloroethane	5.0	5.0
P	1,1,2,2-Tetrachloroethane	5.0	5.0
	Tetrachloroethene	5.0	5.0
C K	Toluene	5.0	5.0
S	Toluene-d8	----	----
	1,2,3-Trichlorobenzene	5.0	5.0
	1,2,4-Trichlorobenzene	5.0	5.0
	1,1,1-Trichloroethane	5.0	5.0
	1,1,2-Trichloroethane	5.0	5.0
K	Trichloroethene	5.0	5.0
	Trichlorofluoromethane	5.0	5.0
	1,2,3-Trichloropropane	5.0	5.0
	1,2,4-Trimethylbenzene	5.0	5.0
	1,3,5-Trimethylbenzene	5.0	5.0
C	Vinyl chloride	2.0	2.0
	Total Xylenes	5.0	5.0
	Acrolein	100.	100.
	Methyl Iodide (iodomethane)	10.	10.
	Carbon Disulfide	10.	10.
	Acetone	100.	100.
	Allyl chloride	10.	10.
	Acrylonitrile	100.	100.
	Vinyl Acetate	5.0	5.0
	Chloroprene	10.	10.
	Propionitrile	10.	10.
	2-Butanone (MEK)	100.	100.

Table 1 continued.

QC Use	Analyte	Aqueous RL (ug/L)	Non-Aqueous RL (ug/Kg)
	Methacrylonitrile	10.	10.
	Methyl Methacrylate	10.	10.
	2-Chloroethyl Vinyl Ether	10.	10.
	cis-1,3-Dichloropropene	5.0	5.0
	trans-1,3-Dichloropropene	5.0	5.0
	Ethyl Methacrylate	10.	10.
	4-Methyl-2-pentanone (MIBK)	50.	50.
	Methyl-tert-butyl ether	10.	10.
	2-Hexanone	50.	50.
	trans-1,4-Dichloro-2-butene	5.0	5.0
	Pentachloroethane	10.	10.
S	Dibromofluoromethane	---	---

QC (Quality Control) Uses:
- T - Mass Spectrometer Tuning Performance Compound
- P - System Performance Check Compound (SPCC)
- C - Calibration Check Compound (CCC)
- S - Surrogate Compound
- I - Internal Standard for Quantitation
- K - Matrix Spike Compound

1.3. Several analytes are listed by their common name in EPA methods while others are listed by their proper IUPAC names. Clients may use either the common or IUPAC name when requesting analysis. This can confuse analysts who are only familiar with the proper IUPAC nomenclature taught in Organic Chemistry courses. It is important to understand both types of naming so that we assure that the correct analysis is being performed.

The common and proper names of some of the analytes are listed below. Common names are listed in Table 1.

Common Name	Proper Name
Chloroform	Trichloromethane
Bromoform	Tribromomethane
Vinyl chloride	Chloroethene
Methylene chloride	Dichloromethane

1.4. It is a common practice to use the following acronyms when referring to chlorinated ethenes and ethanes. The third letter of the acronym (A or E) indicates whether the compound is an ethane or ethene.

Dichloroethane	(DCA)
Dichloroethene	(DCE)
Trichloroethane	(TCA)
Trichloroethene	(TCE)
Tetrachloroethane	(PCA)
Tetrachloroethene	(PCE)

The common name for tetrachloroethene is perchloroethene. The prefix per- means "containing the largest possible proportion of an element". Since the largest number of chlorines possible in a chlorinated ethene is four, perchloroethene contains four (or tetra-) chlorine atoms. The acronym PCE is used for tetrachloroethene to differentiate it from the acronym for trichloroethene, TCE. The acronym PCA is used for tetrachloroethane to differentiate it from the acronym for trichloroethane, TCA. However, the greatest number of chlorine atoms possible in a chlorinated ethane is six, not four. Regardless, the acronym PCA is used to denote tetrachloroethane even though perchloroethane is hexachloroethane.

Dichloroethane may sometimes be referred to as EDC (ethane, dichloro-) as well as DCA. Similarly, the acronym for dibromoethane is EDB (ethane, dibromo-).

2. SUMMARY OF METHOD

The volatile compounds are introduced into the gas chromatograph by the purge and trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol extract is combined with organic free reagent water. It is then analyzed by purge and trap GC-MS.

In the purge and trap process, an inert gas is bubbled through the solution, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3. SAFETY

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures prior to the use of any chemical. In all cases, both the applicable Material Safety Data Sheet (MSDS) and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the TestAmerica Safety Manual. The bottle labels also provide important information that must be noted. Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much (or more) care as any of the materials used in this method due to the unknown nature of their composition. Also, the equipment utilized by this method contain areas of both high temperature and potentially lethal voltage. Care must be taken whenever performing maintenance on these systems.

4. REAGENTS AND MATERIALS

The following equipment and materials, or their equivalent, are recommended for this method. Equipment and materials are considered equivalent if, with their use, the analytical and QA/QC requirements in this SOP can be met.

4.1. Apparatus

4.1.1. Microsyringes - 0.5 uL, 1.0 uL, 2.0 uL, 5.0 uL, 10 uL, 25 uL, 100 uL, 250 uL, 500 uL, and 1,000 uL. Whenever possible, choose the syringe size that maximizes volume usage of the syringe for most effective results.

4.1.2. Syringe valve - Two-way, with Luer ends (three each) if applicable to the purging device.

4.1.3. Syringe - 5 mL, gas-tight with shutoff valve.

4.1.4. Balances - Top-loading balance capable of weighing 0.1g and an analytical balance capable of weighing 0.001g.

4.1.5. Glass scintillation vials - 20 mL, with screw caps and Teflon liners.

4.1.6. Volumetric flasks - 5 mL, 10 mL and 100 mL, class A with ground-glass stoppers.

4.1.7. Vials - 1 mL Supelco #3-3293M.

4.1.8 Mininert Valve - for 1 mL vial, Supelco #3-3301M.

4.1.9. Vials, amber - 10 mL, Shamrock #3739A, 50 mL Shamrock #3745A.

4.1.10. Mininert Valve - for 10 mL and 50 mL vial Shamrock #306.

4.1.11. Spatula - Stainless steel.

4.1.12. Disposable pipets - Pasteur.

4.1.13. Heater - capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C. This is only required for low level soil analysis.

4.1.14. Purge and trap device - The purge and trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.1.14.1. The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles. The purge gas must be introduced at 1.5 cm below the water level. Use the following type of purge vessels:

Water- Tekmar 5 mL fritted sparger 14-0042-024 or 14-3544-124.
Medium Soil- Tekmar 5 mL fritted sparger
Low Soil- Sample is purged directly in VOA vial.

4.1.14.2. Trap: Supelco Catalog #2-166M (trap K). Before initial use, the trap must be conditioned for 1 hour by baking at 270°C with an inert gas flow of at least 20 mL/min. Prior to daily use, bake the trap for 10 minutes at 270°C.

4.1.14.3. The desorber should be capable of rapidly heating the trap to 270°C for desorption.

4.1.15. Gas Chromatograph - Mass Spectrometer System:

4.1.15.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. Hewlett-Packard Model 5890 is used.

4.1.15.2. Column J&W DB-624.

4.1.15.3. Mass spectrometer - Capable of scanning from 35-300 amu every 2 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 2 when 50ng of 4-Bromofluorobenzene (BFB) are injected through the gas chromatograph inlet. If the tuning criteria cannot be met, inform your Supervisor and do not analyze standards or samples.

4.1.15.4. GC-MS interface - jet separator, or an open split fused silica interface. Open split fused silica interface Hewlett Packard Cat. # 05971-20590 (restrictor splitter). This is required to meet the performance specifications listed in Sw-8260A.

4.1.15.5. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC-MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Also, it must have the capacity of time stamping all data generated with the correct date and time. It is the responsibility of the GC-MS Section Supervisor to ensure that the data system's clock is correct within 1 minute of the local true time. Absolutely no adjustment shall be made to this clock so as to misrepresent the actual date and/or time of analysis.

4.2. Reagents

4.2.1. Reagent grade chemicals shall be used in all tests.

4.2.2. Reagent water. Must not contain interferences at or above the RL except for the common laboratory solvents (methylene chloride and toluene) which must be less than 25ug/L. If a source of organics-free water is not available, it is necessary to remove the organics from the reagent water. The following are possible techniques for purifying water. In addition, water may be purchased.

4.2.2.1. A water purification system (Millipore Milli-Q Plus with the Organex-Q cartridge or equivalent) may be used to generate reagent water.

4.2.2.2. Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free nitrogen or air through the water for one hour. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap. Alternatively, a continuous water distillation system may be used for this part of the purification.

4.2.2.3. Use a charcoal filter to remove organics. The filter should be connected immediately prior to, or after, the faucet.

4.2.3. Methanol, CH_3OH. Fisher Purge and Trap grade methanol (or equivalent.) Store apart from other solvents.

Caution: Methanol (methyl alcohol) is toxic by ingestion, inhalation and absorption. Gloves and safety glasses should be worn to avoid contact with eyes and skin. Avoid inhalation by working with this solvent in a fume hood. Many of the following standards are prepared in methanol.

NFPA Information: Health = 3, Flammability = 3, Reactivity = 1, Contact = 1.

4.3. Standards Reagents and Preparation

Caution: The following standards may contain one or more known or suspected carcinogens. Read all precautionary information supplied with the standards. Gloves and safety glasses should be worn to avoid contact with eyes and skin. Any use of these standards in a manner that causes the release of vapors into the laboratory atmosphere should be conducted within a fume hood. Hoods are classified as designated areas when working with carcinogens. The standards may be supplied in methanol. See note of caution above.

4.3.1. Standards storage. All standard solutions will be stored so as to minimize headspace. Standards must be stored in a freezer at -10°C to -20°C. These may not be stored in the same freezer with BNA or pesticides standards or sample extracts.

4.3.2. Manufacturers of standards sometimes will change the concentration and composition of standards. ALWAYS read the literature provided with the standard so that the concentration and composition of the working standard is known. Whoever creates the working standard is responsible for informing other analysts of changes in the standard concentration or composition. Each analyst in turn is responsible for ensuring that calibration and ID files are correct. Prior to creating each standard the analyst should calculate the final concentration of the standard. Do not use the volumes recorded in the standard logbook for the previous standard and assume the volumes required are the same.

4.3.3. Surrogate Standards.

4.3.3.1 Surrogate mother solution (MoSurr).

Dibromofluoromethane: Supelco Cat.# 4-8077
d8-Toluene: Supelco Cat.#4-8593 or Aldrich Aldrich Cat.# 15,199-8
Bromofluorobenzene: Supelco Cat.# 4-8800 or Aldrich Cat.# B6,720-1
1,2-Dichloroethane-d4: Chemservice Cat. #F836

Surrogate mother concentration is 50,000 ug/mL. The surrogate working solution concentration is 25 ug/mL. The mother solution is prepared by weighing up 0.25 grams of each surrogate standard into 5 mL of MeOH. The working solution is prepared by taking 250 uL of mother solution to 50 mL in MeOH.

4.3.4. Internal Standards.

Fluorobenzene: Aldrich Cat.# F600-1
Chlorobenzene-d5: Aldrich Cat.# 17,660-5
1,4-Dichlorobenzene-d4: Supelco Cat.# 4-8049 or
Aldrich Cat.#32,933-9

Internal Standard mother concentration is 50,000 ug/mL. The internal standard working solution concentration is 25 ug/mL. The mother solution is prepared by weighing up 0.25 grams of each internal standard into 5 mL of MeOH. The working solution is prepared by taking 250 uL of mother solution to 50 mL in MeOH.

4.3.4.1. 25 ug/mL Combined Internal Standard Surrogate Solution (SURRISTD) For 2050 with a 10 uL loop.

4.3.5. Initial Calibration Verification Standard. The ICVS is a calibration standard analyzed immediately after a calibration curve to verify the calibration curve. The ICVS must be from a different source than the Mother solution (4.3.6.). If a second source is not available, use a different lot number as an ICVS. If a second source or lot number is not available, ICVS analysis is not required. Every effort should be made to obtain ICVS standards. The ICVS Mother should be identical to the 200mg/L VSTD in 4.3.6. A 50 ppb working standard is analyzed as the ICVS.

4.3.6. 200mg/L Calibration Standard (VSTD). The following standards may be used to prepare the calibration standard:

4.3.6.1. Cool the following standards and a 1.0 ml syringe in the freezer.

Restek 30006-500 VOA Cal Mix #1	5000 ug/mL
Restek CLP VOA Cal 2000 Mega Mix	2000 ug/mL
Restek 30010-500 VOA Cal Mix #5	2000 ug/mL
Restek Custom VOA Cal Mix #1A	2000 ug/mL
Restek Acrolein/Acrylonitrile	20,000 ug/mL
Restek Dichlorodifluromethane	2000 ug/mL
Supelco Appendix IX Custom Mix#6	2000 ug/mL
Supelco Appendix IX Custom Mix#7	2000 ug/mL
NET VOA Custom Mix	5000 ug/mL
Restek Chloroprene	5000 ug/mL

Also cool a 10 mL vial containing 1.2 mL of methanol with mininert cap attached in the freezer. One at a time take each ampule, crack it and add the necessary amount of standard to the vial through the mininert valve. For NET VOA Custom Mix and Chloroprene, use 400 uL. For each of the remaining standards use 1.0 mL. Invert the standard slowly five times to mix. Label

this calibration mother solution as VSTD.

4.3.6.2. To prepare NET VOA Custom Mix, to a 10 mL volumetric add 50 mg of the following compounds:

Propionitrile
1,2,4-Trimethylbenzene
Hexane
1,1-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane

Bring to volume with methanol. Invert standard slowly five to six times. Transfer quickly to a 10 mL mininert vial.

4.3.6.3. An additional standard used in the preparation of 8260 calibration standards is listed below:

Bromochloromethane 200 ug/mL

To prepare a 2000 ug/mL solution, add approximately 5 mL of methanol to a 10 mL volumetric. Add 20 mg of Bromochloromethane and bring to volume with methanol. Mix by inverting the volumetric five to six times. Add 9 mL of methanol to a 10 mL mininert vial. Transfer 1 mL of the 2000 ug/mL solution of Bromochloromethane to the mininert vial to give a 200 ug/mL solution.

These standards can not be kept for more than 6 months. Do not hesitate to replace the standard more frequently if you suspect it has degraded. Standards can be divided into small vials (1 mL or 2 mL) for storage. Dividing the standard may help to preserve the standard integrity and reduce the frequency with which new standards must be made. Monitor the analyte responses daily. A common form of degradation is when the gases volatilize into the vial's headspace and the concentration of the gases in the standard decreases. The response for the gases will decrease compared to previous calibrations with the same standard. Do not use a standard that has degraded for performing a new initial calibration. The life of the standards will be maximized if they are always returned promptly to the freezer for storage. Do not allow standards to warm to room temperature.

4.3.7. Matrix Spike, MVS, LSC Solution (VOA-QC). The Mother solutions used for Laboratory Control Samples (LCSs) and Method Validation Study (MVS) analysis are identical in composition and concentration to the Mother Solutions in section 4.3.6. This solution can also be used for Matrix Spikes, or a different solution can be prepared. The Mother Solutions for LCS, MVS and MS spiking should be prepared from a different source than the calibration Mother Solution in section 4.3.6.

4.3.7.1. Matrix Spikes. Matrix spikes are spiked client samples. This differs from Laboratory Control Standards (section 4.3.7.3) which are spiked reagent water. The matrix spikes are prepared by adding the spiking solution to the sample aliquots prior to their analysis. The matrix spiking solution should contain a representative subset of the target analytes. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene and benzene. (These compounds are indicated in Table 1 with the letter K.) The LCS spiking solution, containing all target analytes may also be used for matrix spiking. The concentration of each of the matrix spike analytes should be 20 ug/L in 5 mL of water.

4.3.7.2. Method Validation Sample (MVS). The MVS is used to validate the analytical method. Four 5mL replicates of reagent water spiked at 20 ug/L. The MVS must contain all reported analytes which are present in Table 1.

4.3.7.3. Laboratory Control Standard (LCS). The LCS is used to evaluate the MS/MSD results when MS/MSD recovery limits are exceeded. The LCS is 5 mL of reagent water spiked at 20 ug/L. The LCS must contain all reported analytes which are present in Table 1. LCSs are used with aqueous, low-level, and medium-level non-aqueous preps.

4.3.8. 25mg/L Bromofluorobenzene standard (BFB) (optional for 2016). Purge 2.0 uL of this solution to provide 50 ng on column for BFB Tuning criteria.

5. INTERFERENCES

5.1. Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

5.2. Samples can be contaminated by diffusion of volatile organics (particularly Methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. Some clients may include a field blank prepared from reagent water which is carried through the sampling and handling protocol to serve as a check on such contamination. At the client's request some labs may provide trip blanks. Since contamination of field and trip blanks may be due to factors outside of the laboratory, the client should evaluate the results.

5.3. Charcoal is very effective in absorbing volatile organics. If a sample is expected to be highly contaminated place the pair of 40 mL VOA vials into a resealable sandwich bag (baggie) with 5 g of fresh activated charcoal to minimize cross-contamination among samples and blanks. Discard the baggies and charcoal after each use. Some analysts will place a beaker of charcoal in sample and/or standard refrigerators to absorb contamination.

5.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of reagent water in the same purge vessel position to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample is analyzed. For this reason, sample screening is highly recommended. The laboratory where volatile analysis is performed should be completely free of ambient atmospheric solvents which are analytes.

6. ANALYTICAL PROCEDURE

6.1. Instrument Preparations

6.1.1. Recommended Mass Spectrometer Conditions

Electron energy:	70 volts (nominal)
Mass range:	35-300 amu
Scan time:	To give 5 scans/peak but not to exceed 5 sec/scan. Set A/D to 8 (2 to 3rd power) or 16 (2 to 4th power), integration time to 25 micro seconds

6.1.2. Recommended GC Operating Conditions

Initial column temperature:	35°C
Initial column holding time:	5.0 minutes
Column temperature program 1:	7°C/minute
Final column temperature 1:	70°C
Final column time 1:	0.0 minutes
Column temperature program 2:	10°C/minute
Final Column Temperature 2:	200°C
Final column time 2:	6 minutes or greater
Injector temperature:	200°C
Source temperature:	See manufacturer's recommendation
Transfer line temperature:	250°C
Carrier gas:	Helium, flow rate is column dependent

6.1.3. Recommended Purge and Trap Conditions

Purge Flow:	40.mL/minute
Purge Time:	11 minutes
Purge Temperature:	Ambient
Cooldown:	4°C (w/Moisture Control Module (MCM))
MCM Temperature:	90°C (if used)
Dry Purge Time:	3 minutes (Without MCM) 3 minutes (with MCM)
Preheat (Low soil):	2 minutes
Trap Temperature:	30 to 35°C
Desorb Preheat Temperature:	245°C
Desorb Temperature:	250°C
Desorb Time:	4.0 minutes
Bake Temperature:	260°C
Bake Time:	5 Minutes

6.1.4. Condition the trap initially for 1 hour prior to use by baking at 270°C. With a minimum purge flow of 20 mL/min. Allow the trap to cool to 35°C and measure the purge flow. Adjust the purge flow to approximately 40 mL/min if necessary. Record the flow rate in the instrument logbook. Condition the trap daily for 10 min by baking at 270°C with the column at 200°C.

6.1.5. GC BFB Instrument Conditions - Each GC-MS system must be tuned to meet the criteria in Table 2 for a 50 ng injection or purge of 4-bromofluorobenzene (BFB). Analyses must not begin until these criteria are met. BFB analysis may be performed with GC conditions which allow for a rapid runtime. The following conditions are suggested.

Initial column temperature	70°C
Initial column holding time	1 minutes
Ramp rate program 1	13°C/minute
Final column temperature	200°C
Final column holding time	1 minute
Runtime	12 minutes

Table 2. Bromofluorobenzene Tuning Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95.
75	30 to 60% of mass 95.
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95.
173	<2% of mass 174.
174	>50% of mass 95.
175	5 to 9% of mass 174.
176	>95% but <101% of mass 174.
177	5 to 9% of mass 176.

6.2. Method Validation Sample (MVS) Analysis.

6.2.1. This method must be validated by demonstrating that acceptable precision and accuracy can be obtained.

6.2.2. Analyze four MVSs containing the analytes listed in Table 5 at 20 ug/L for a 5 mL purge or at 5 ug/L for a 25 mL purge. Other analytes may be at greater concentrations if they are not easily detected at 20 ug/L in 5 mL or 5 ug/L in 25 mL. The MVSs must be analyzed one after the other and quantitated using the same calibration. Calculate the average recovery (x) and the standard deviation of the recovery (s) for the four MVSs. The results must meet the mean (x) and standard deviation (s) limits in Table 5 to validate the method. The method validation is required to performed on each GC-MS performing this method, and by each analyst performing this method. Each analyst is not required to perform method validation on every instrument he uses for analysis. Validation should be repeated whenever a significant change in the procedure or equipment is made which would render the previous MVS invalid. For example, replacing a Tekmar LCS-2 with an LCS-2000 would require a Method Validation Study. Replacing a trap or column with an identical one would not require an MVS.

6.2.3. One of the MVSs may be used as a point of an initial calibration curve.

6.2.4. The MVSs may be analyzed at ambient temperature or 40°C. They must be analyzed at the same temperature as the calibration standard used to quantitate them.

6.3. Initial Calibration Curve

The criteria in Table 2 must be met for BFB prior to the analysis of any curve. All points for a curve must be injected within 12 hours of the BFB injection.

A set of at least five calibration standards is required for an initial calibration. One standard should contain each analyte of interest at concentrations approaching but greater than the method detection limits; the other calibration standards should be at concentrations that define the range of the method. The directions given below are for 5 mL of water being purged.

Table 3.

CALIBRATION SOLUTION PREPARATION (Volume of Standards per 200 ml reagent water)		
Calibration Conc. ug/L	VSTD uL	Bromochloromethane uL
5	5	5
10	10	10
20	20	20
50	50	50
100	100	100
150	150	150

6.3.1 Ambient Temperature Calibration Curve for Waters. Follow the instructions above to prepare 200 mL of each calibration solution. The uL amounts of each mother solution can be adjusted if smaller or larger volumes of calibration solutions are needed.

6.3.2. For an Archon, standards must be made in 50 mL volumetric flasks and transferred to 40 mL VOA vials for analysis. Add approximately 40 mL of reagent water into a 50 mL volumetric flask. Measure the required amount of standard with a gas-tight syringe. Insert the syringe needle into the flask so that the tip of the needle is 2 to 3 cm below the surface of the water and inject the standard. Dilute to the mark with reagent water. Invert slowly three times to mix. Decant and discard the volume of standard in the neck of the flask. When using an Archon this method should be used and the standard should be transferred into a VOA vial with minimal agitation for analysis. For low level soils, transfer 5 mL to a VOA vial for analysis. For medium-level, follow aqueous directions.

6.3.3. Quantitate all standards and assure that all compounds present are found by the data system. All "Q-Values" should be greater than 80 for the midrange standard. If any are less than 80 edit the ion ratio criteria in the data system to reflect current results.

6.3.4. The average RF must be calculated and recorded for each compound. RF is calculated as follows:

$$RF = (A_x)(C_{is}) / (C_x)(A_{is})$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

6.3.5. System Performance Check Compounds (SPCCs). A system performance check should be made before a calibration curve is used. The five SPCCs (indicated by a P in Table 1) are checked for a minimum average response factor. The minimum acceptable average RF for these compounds are listed below. The SPCC compounds are used to check compound instability and degradation caused by contaminated lines or active sites in the system.

SYSTEM PERFORMANCE CHECK COMPOUNDS
(Minimum response factors)

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	>0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

The SPCC compounds are used to check compound instability and degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

6.3.5.1. Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast. If the trap temperature is lowered to 30°C the chloromethane response may increase. A low chloromethane RF may indicate that the volatile standard has degraded and needs to be replaced.

6.3.5.2. Bromoform - This compound is one of the compounds most likely to be purged poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect this RF. In addition, response of the quantitation ion (mass 173) is directly affected by mass spectrometer tune. Maximize high mass sensitivity (the 131 and 219 ion of PFTBA) so as to increase the 174 ion of BFB to between 80% and 99%. This will improve the relative sensitivity of bromoform.

6.3.5.3. Tetrachloroethene, cis-dichloropropane, and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

6.3.6. Calibration Check Compounds (CCCs). Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for each CCC. (CCCs are indicated by a C in Table 1.) The percent RSD is calculated as follows:

$$\%RSD = \frac{s}{x} \times 100$$

where:

RSD = relative standard deviation
x = mean initial RF for a compound
s = standard deviation of RFs for a compound

$$s = \sqrt{\sum_{i=1}^{n} \frac{(y_i - y_{avg})^2}{n - 1}}$$

The RSD for each individual CCC must be less than 30%. This criterion must be met for the calibration to be valid.

6.3.7. Linearity- If the % RSD for any compound in the initial calibration is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

6.3.7.1. If any %RSD for any analyte is greater than 15% a calibration curve using first or second order regression must be employed to calculate the RF to be used for sample quantitation. If linear regression is employed, correlation coefficient must be greater than 0.990 (r2 = 0.980) for the calibration to be considered valid.

6.3.8. If a standard saturates at the highest level this point should not be included in the curve. Saturation is evident by a

decreasing RF at increasing concentrations. A minimum of five calibration standards are required. Recalibration at a lower level is required if after dropping the high standard there are not five points. It is not permissible to drop the lowest point (nearest the detection limit) because of the importance of low level concentrations for volatiles analysis.

6.3.9. Meta- and para-xylene are isomers which coelute. They are identified and quantitated as one peak. Some manufacturers will put both meta- and para-xylene in their mix, while others will include either meta- or para- but not both. Since we cannot differentiate between these isomers, all sample results will be reported as meta- and para-xylene, or as total xylenes, regardless of whether or not both of the isomers are present in the standards. It is common practice to sum the meta-, para- and ortho-xylene values and report a single value for total xylenes.

6.3.10. Other structural isomers that provide similar mass spectra should be identified as individual isomers if the height of the valley between the two isomer peaks is less than 25% of the sum of the two peaks.

6.3.11. After a successful initial calibration measures must be taken to ensure that the system is contaminant free. Analyze a blank after the final standard analysis. The blank must meet the criteria in section 6.4.3.2. If the criteria are not met clean the position and repeat a blank at that position until it passes. Proceed to section 6.5 to analyze samples for a period not to exceed 12 hours from the last BFB tune, at which time the tune and the calibration must both be verified again. (See section 6.4.)

6.3.12. Review the midlevel standard carefully to ensure all analytes were correctly identified and integrated. If there are any problems found with an analyte in the midpoint, check this analyte for the remaining points.

6.3.13. The analysis of an independent reference standard, or ICVS, is required immediately following each curve. The ICVS should be quantitated with the average response factors from the curve. If the quantitation results are not within +/- 30% it can be re-analyzed. If a successful ICVs cannot be analyzed a new initial calibration curve must be analyzed for the compounds that are out of control. Analytical results can not be accepted until an acceptable ICVs has been analyzed. Document all ICVS results.

6.3.14. It is not always possible, or practical, to have all analytes calibrated in a a single calibration run. If necessary it is acceptable to use two separate analyses to calibrate a single point.

6.3.15. Retention time windows are to be set at +/- 0.5 minutes relative to the mean RT of each compound in the initial calibration curve.

6.4. Daily System Verification

6.4.1. The system must be verified to be in control daily. The

following is the order in which a 12-hour sample analysis shift is conducted:

6.4.1.1. The 12 hour clock starts with the injection time of the successful BFB analysis. All criteria in Table 2 must be met.

6.4.1.2. Continuing calibration standard analysis. All criteria in section 6.4.2 must be met.

6.4.1.3. Method blank analysis. All criteria in 6.4.3.2 must be met.

6.4.1.4. Laboratory Control Standard (20ug/L), one per batch of 20 samples, or less, for aqueous, low-level and medium-level non-aqueous.

6.4.1.5. Until the end of the 12 hours sample and MS/MSD analyses may be performed. MS/MSD set is required one per batch of 20 samples or less of a single matrix.

6.4.1.6. Prior to any analysis, purge 50 ng of the BFB standard. All of the criteria given in Table 2 must be met before standard or sample analysis begins. This hardware tune must be demonstrated at the beginning of each 12-hour shift. See section 6.1.5 for requirements.

6.4.2. Continuing Calibration Verification Standard (CCVS). The initial calibration curve for each compound of interest must be verified at the beginning of every 12 hour sequence. This is accomplished by analyzing a midlevel calibration standard according to section 6.3.1 or 6.3.2 and meeting the criteria listed below.

6.4.2.1. All SPCCs must meet their minimum RF requirements.

6.4.2.2. Calculate % Drift using the following equation for all CCCs listed in Table 1:

$$\% \text{ Drift} = (Ci - Cc/Ci) \times 100$$

Ci = Calibration Check Compound standard concentration.

Cc = Measured concentration using selected quantitation method.

If the percent drift for each CCC is less than 20%, the initial calibration is assumed to be valid and sample analysis may begin.

6.4.2.3. If the system fails these criteria, determine if some form of system maintenance is necessary. Some of the more common sources of problems are a bad trap, a change in purge flow, a significantly different MS tune, an improperly prepared standard or a degraded standard. Perform the necessary corrective action and repeat the standard. If the source of the problem cannot be determined the instrument must be recalibrated as in 6.3. Before any analytical results can be submitted an acceptable CCV or calibration curve must be analyzed. All analytical results associated with an unacceptable CCV must be re-analyzed.

6.4.2.4. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made.

6.4.2.5. The extracted ion current (EIC) areas for the internal standards shall also be monitored for each analytical batch. The EIC area for any of the internal standards (based upon those in the check standard) cannot change by greater than a factor of two (-50% to +100%.) Any sample for which it does must be re-analyzed.

6.4.3. Method Blanks

6.4.3.1. A method blank must be prepared and analyzed in an identical manner as the samples. There should be a method blank for each of the procedures: aqueous, low-level and medium-level non-aqueous. See sections 6.4.3.6 through 6.4.3.8 for preparation directions.

6.4.3.2. For a blank to be "in control" all analytes must not be detected above the RL. (see section 7.6). The term "analytes" applies only to those compounds for which analysis is being performed. For example, if the analysis is for benzene only, other compounds may be detected in the blank above the RL.

6.4.3.3. Any "out of control" blank must be reviewed carefully with due consideration of the client's needs. All samples must be re-analyzed if the blank contamination exceeds the acceptance limits and the analyte in question was detected in the samples. If samples cannot be re-analyzed because of insufficient sample volume the data will need appropriate texting.

6.4.3.4. Sample results must be flagged if any reported analytes were also detected in the blank above the reporting limit.

6.4.3.5. If the internal standard requirements listed in 6.4.2.4 and 6.4.2.5 or the surrogate recovery limits listed below are exceeded contact your supervisor. The blank and/or all associated samples must be reanalyzed to confirm the matrix effect. An MS/MSD may also be used to confirm a matrix effect.

Surrogate Limits:	Aqueous	Non-Aqueous
Dibromofluoromethane	86-118	80-120
Toluene-d8	88-110	81-117
Bromofluorobenzene	86-115	74-121
Dichloroethane-d4	80-120	80-120

Statistical control limits must be generated for surrogates. Using a data base of 20-30 points calculate control limits from ± 3 standard deviations from the mean. The limits should be updated yearly.

6.4.3.6. Aqueous method blank. To 5.0 mL of reagent water the Archon adds 1.0 uL of the SURRISTD standard. Analyze according to conditions outlined in 6.1 purging at ambient temperature.

6.4.3.7. Low soil method blank. Add 5 mL of reagent water to a VOA vial. Surrogates and internal standards are added by the Archon. Analyze according to conditions outlined in 6.1, purging at 40°C.

6.4.3.8. Medium soil method blank. To a 20 mL vial add 4.5 mL of methanol and 0.5 mL of MEDSURR. Add 100 ul of this mixture to 50 mL of reagent water. Add 10 uL of ISTD to the reagent water. Analyze according to the conditions outlined in 6.1, purging at ambient temperature.

6.4.3.9. If the blank criteria in 6.4.3.2 is exceeded steps must be taken to determine the source of contamination. The following are suggested steps:

(1) Regenerate the reagent water and reanalyze the method blank.

(2) Analyze the reagent water without surrogates or internal standards to determine if the standards are the source of contamination.

(3) Analyze 1/2 the volume of reagent water to determine if the contamination is in the water.

(4) Prepurge the purge vessel prior to loading the blank to determine if the contamination is in the air.

(5) Position the blank in another purge vessel to determine if a particular position is contaminated.

(6) For medium-level blank contamination it will be necessary to re-extract the blank and any associated samples to achieve the criteria in 6.4.3.2. This will help confirm or eliminate the methanol as the source of the contamination.

6.4.4. LCS and MS/MSD analysis are required one per batch of 20 samples or less. It is highly recommended that the LCS be analyzed immediately following the blank, prior to samples. The LCS results should be evaluated immediately to ensure that all data will be reportable regardless of the MS/MSD results. See section 6.5.7 concerning evaluation of the LCS results.

6.4.5. When aqueous sample volume is limited, it may not be possible to perform a MS and/or a MSD. When this is the case,

indicate so in the instrument logbook. If possible perform an MS and an LCS analysis. If there is not enough sample volume for a MS simply perform a single LCS analysis. Duplicate LCS analysis is not required. Every effort should be made by appropriate personnel to obtain adequate aqueous sample volume from clients for MS/MSD analysis.

6.5. Sample and Quality Control Indicator (QCI) Analysis

6.5.1. Refer to section 6.4.3.5. regarding surrogate requirements. Refer to section 6.5.7. regarding Matrix Spike, Duplicate, and Laboratory Control Spike acceptance criteria and corrective action guidance.

6.5.2. The screening of samples is highly recommended prior to GC-MS analysis.

6.5.3. Water Samples.

6.5.3.1. Inspect all aqueous samples for sediment. If there is any sediment in the VOA vial decant the sample into another vial for analysis.

6.5.3.2. The VOA vial can be directly placed in the Archon and analyzed under the conditions outlined in Section 6.1.

6.5.3.3. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range the sample must be re-analyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

6.5.3.4. When a highly contaminated sample is analyzed, this analysis must be followed by a water blank analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences. Be alert for potential carryover into subsequent samples. Re-analyze any samples which are suspected of being contaminated by carryover.

6.5.3.5. Analyze a 20ug/L LCS. See section 6.5.7. for acceptance criteria.

6.5.3.6. The extracted ion current (EIC) areas for internal standards must be within -50% to +100% of the 50ug/L continuing calibration standard areas. If the internal standard areas for a sample are not within this range the sample must be reanalyzed once. If upon reanalysis the internal standard areas are outside of the control limits, provide both sets of data to your Supervisor for review. A third analysis is not required but may be recommended by your Supervisor.

6.5.3.7. The analyst should consider the possibility that a leak caused low areas. Otherwise, a matrix effect may have altered internal standard areas. Inspect the total ion chromatogram to see if any large peaks are present which may have caused interference. Also, it is possible for samples to contain sufficient non-volatile organics to cause purging problems

without a visible peak. Most notably leachates fall into this category. Foaming of samples is another common cause for low internal standard areas.

6.5.3.8. If it is determined that the problem is a matrix effect, the sample must be reanalyzed once at a dilution to diminish the matrix effect. Severe matrix effects may not be resolved with dilution. Submit both sets of data for review.

6.5.3.9. If no apparent reason can be found, reanalyze the sample without dilution once. If upon reanalysis the internal standard areas are again out of control then both sets of data should be submitted for review. Otherwise, submit only the reanalysis data.

6.5.3.10. Surrogate recoveries must meet limits in section 6.4.3.5. If surrogate recoveries do not meet the limits reanalyze the sample once. If it is suspected that a matrix effect caused surrogate recoveries to be beyond the limits, reanalyze the sample at a dilution. If upon reanalysis the surrogate recoveries are outside of the control limits, provide both sets of data to be reviewed.

6.5.3.11. Severe matrix effects may be difficult to reproduce. If internal standard or surrogate recovery problems can not be duplicated, do not analyze samples a third time without contacting your Supervisor.

6.5.3.12. If quality control requirements can not be met for any of the indicators listed in Section 6.5.3 after re-analysis the best data is reported along with appropriate flags to the client. It is up to the client to determine the usability of the data.

6.5.4. Water-miscible liquids/medium level water samples.

6.5.4.1. Perform dilutions using volumetric flasks whenever possible. Always start with a volumetric partially filled with water and insert the needle at least 2 cm below the surface. Fill to mark and mix by slowly inverting three times. Pour off the liquid in the neck of the volumetric. An aliquot of the rest may be delivered to a VOA vial for analysis, or delivered to another volumetric for secondary dilutions. Once delivered to the VOA vial, the sample is ready for addition of internal and surrogate standards. When performing dilutions of great magnitude, extreme care must be taken so as to avoid contamination, particularly through the use of contaminant free water. Due to the magnitude of the dilution involved even small levels of contamination will cause the reporting of spurious results of very high concentration.

6.5.4.2. If there is any doubt about the homogeneity of a sample, use a greater sample volume and perform a secondary dilution. It may be appropriate to use < 1 mL of sample if it is known to be homogeneous.

6.5.4.3. Proceed with analysis for low waters.

6.5.5. Low level sediment/soil and waste samples.

It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. This method is designed for samples containing individual purgeable compounds of <1 mg/Kg. It is limited to sediment/soil samples and waste that is of similar consistency (granular and porous). The low level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standard. Analyze all reagent blanks and standards under the same conditions as the samples.

6.5.5.1. Use 5.0 g sample if the expected concentration is <0.1 mg/Kg. Use 1.0 g sample for expected concentrations between 0.1 and 1 mg/Kg.

6.5.5.2. Continuing calibration standards for low level soils must be purged at 40°C. Prepare the 50 ug/L standard as described in 6.3.2.

6.5.5.3. The sample (for volatile organics) consist of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in section 6.5.5.1 into a tared purge device (test tube or VOA vial). Note and record the actual weight to the nearest 0.1 g.

6.5.5.4. Add 5 mL of reagent water to the 40 mL VOA vial containing the sample. Surrogate and internal standard are added automatically by the Archon prior to purging.

6.5.5.5. Purge according to conditions outlined in section 6.1 for heated purge at 40°C.

6.5.5.6. If any analyte is detected at a concentration greater than the upper calibration point (usually 200 ug/L), dilution is required. If a 1 g sample amount yields analyte concentrations greater than the upper calibration limit, the medium level soil method must be performed.

6.5.5.7. For low-level sediment soils LCS, add 0.4 uL of VOA-QC to 5 mL of reagent water. Transfer to a 40 mL VOA vial. The concentration is equivalent to 20 ug/Kg. See section 6.5.7 for acceptance criteria.

6.5.5.8. For low-level sediment/soils MS/MSD add 0.4 uL of VOA-QC to 5 mL of reagent water. Transfer to a 40 mL VOA vial containing 5 g of sample. The concentration is equivalent to 20 ug/Kg of each matrix spike standard. See section 6.5.7 for acceptance criteria.

6.5.5.9. Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative

to the dry weight of sediment.

$$\%\text{moisture} = \frac{(\text{g of sample} - \text{g of dry sample}) * 100}{\text{grams of sample}}$$

6.5.5.10. The extracted ion current (EIC) areas for internal standards must be within -50% to +100% of the 50 ug/L heated standard areas. If the internal standard areas for a sample are not within this range the sample must be reanalyzed once. If upon reanalysis the internal standard areas are outside of the control limits, provide both sets of data to your Supervisor for review. A third analysis is not required but may be recommended by your Supervisor.

6.5.5.11. Surrogate recoveries must meet limits in section 6.4.3.5. If surrogate recoveries do not meet the limits reanalyzed the sample once. If it is suspected that a matrix effect caused surrogate recoveries to be beyond the limits, re-analyze the sample at a dilution. If upon re-analysis the surrogate recoveries are outside of the control limits, provide both sets of data to your supervisor for review. A third analysis is not required but may be recommended by your supervisor.

6.5.6. Medium level sediment-soils method.

The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the dilute solution or extract is added to reagent water containing surrogate and/or internal standards. This is purged at ambient temperatures. All samples with an expected concentration of >1.0 mg/Kg should be analyzed by this method. All samples with an expected concentration of >1.0 mg/Kg should be analyzed by this method.

6.5.6.1. The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Using a top-loading balance weigh 5 g of sample if insoluble in methanol or 1 g if soluble in methanol into a 20 mL vial. Note and record the actual weight to 0.1 gram.

6.5.6.2. Quickly add 9.5 mL of methanol. Add 0.5 mL of surrogate standard. Cap and shake or sonicate the vial for 2 minutes. If sonicating, allow the vial to return to room temperature prior to opening.

6.5.6.3. Pipet approximately 1 mL of the extract to a 1 mL GC vial for storage, using a disposable pipet. The remainder may be disposed of. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 uL aliquot of each extracts will give a concentration equivalent to 6,200 ug/Kg of each surrogate standard. Transfer 1 mL of solvent to a separate GC vial for use as the method blank.

6.5.6.4. Use Table 4 to determine the volume of solvent extract to add to the 50 mL of water for analysis. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a medium-level sample, start with 100 uL.

TABLE 4.

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF MEDIUM-LEVEL SOILS/SEDIMENTS	
Approximate Concentration Range	Volume of Methanol Extract
500- 10,000 ug/kg	100 uL
1,000- 20,000 ug/kg	50 uL
5,000-100,000 ug/kg	dilute in volumetric flask
Calculate appropriate dilution factor for concentrations exceeding this table.	

6.5.6.5. Add 100 uL of sample extract and 10 uL of internal standard to 50 mL of reagent water. Proceed to section 6.5.6.6. Final surrogate concentration is equivalent to 50 ug/Kg.

6.5.6.6. Proceed with the analysis as outlined in section 6.1.

6.5.6.7. If for any sample an analyte is detected above the upper calibration limit the sample volume used for the dilution. Dilutions should be made so that the analyte concentration is in the upper half of the curve.

6.5.6.8. The extracted ion current (EIC) areas for internal standards must be within -50% to +100% of the 50 ug/L ambient temperature standard areas. If the internal standard areas for a sample are not within this range the sample must be reanalyzed once. If upon reanalysis the internal standard areas are outside of the control limits, provide both sets of data to your Supervisor for review. If acceptable internal standard areas can not be achieved it should be reported along with the sample results so that the client may determine the usability of the data.

6.5.6.9. Surrogate recoveries must meet limits in section 6.4.3.5. If surrogate recoveries do no meet the limits re-extract and re-analyze the sample once. If it is suspected that a matrix effect caused surrogate recoveries to be beyond the limits, re-analyze the sample at a dilution. If upon re-analysis the surrogate recoveries are outside of the control limits, provide both sets of data to your Supervisor for review. A third analysis is not required but may be recommended by your supervisor. If acceptable surrogate recoveries can not be achieved it should be reported along with the sample results so that the client may determine the usability of the data.

6.5.6.10. Severe matrix effects may be difficult to reproduce. If a surrogate or internal standard result can not be duplicated do not analyze the sample a third time without contacting your Supervisor.

6.5.6.11. Medium soil LCS. Add 500 uL of VSTD (section 4.3.6) and 500 uL of surrogate to a 20 mL vial containing 9 mL of methanol. Sonicate for two minutes. Add 100 uL of this mixture to 50 mL of reagent water. Add 10 uL ISTD, transfer to a 40 mL VOA vial and analyze according to conditions outlined in 6.1. See section 6.5.7 for LCS acceptance criteria.

6.5.6.12. Medium soil MS/MSD. Add 500 uL of VSTD and 500 uL surrogate to a 20 mL vial containing 9 mL methanol and 5 grams of sample. Sonicate for two minutes. Add 100 uL of this mixture to 50 mL of reagent water. Add 10 uL of ISTD , transfer to a 40 mL VOA vial and analyze according to conditions outlined in 6.1. See section 6.5.7 for MS/MSD acceptance criteria.

6.5.7. Matrix Spike and LCS.

6.5.7.1. The criteria in Table 5 is for both aqueous and soil/sediment matrices. The criteria does not apply to "unusual matrices" such as ZHE, waste, paint, etc.

6.5.7.2. All analytes in Table 1, for which analysis is being performed should be spiked in the LCS. The MS should contain a representative subset of these analytes.

6.5.7.3. Additional analytes (expanded list analytes) not listed in Table 5 do not have acceptance limits and are not required to be spiked.

6.5.7.4. Matrix spikes must be spiked at 20 ug/L (20 ug/Kg for non-aqueous). The MS results must be compared to the percent recovery limits (p) in Table 5.

6.5.7.5. If any limit is exceeded for one or more analytes, a LCS must be used to evaluate the possibility of a matrix effect. The LCS should be at 20 ug/L, and at the same temperature as the MS.

6.5.7.6. If the LCS analysis meets the accuracy limits in Table 5 for the analyte(s) of concern, the problem with the MS may be attributed to a matrix effect. All data from the corresponding sample set is reportable. Since the MS is only spiked with a representative subset of the target analytes, analytes not spiked in the MS should also be checked in the LCS when the MS does not meet acceptance criteria. If the MS/MSD are out of control the sample data is appropriately flagged so that the client can determine the data's usability. If the precision between the MS/MSD is out of control then the MS/MSD should be repeated to verify sample inhomogeneity and appropriately noted.

6.5.7.7. If neither the LCS or MS/MSD meet the accuracy limit(s) for the analyte(s) of concern, the results for the analyte(s) are not reportable for the corresponding sample set.

6.5.7.8. The corresponding samples must be reanalyzed after the analysis of a successful LCS or MS set for all analyte results to be reportable.

6.5.7.9. It is highly recommended that the LCS be analyzed and evaluated prior to the analysis of samples to ensure that all sample data will be reportable.

6.5.7.10. Statistical control limits must be generated for matrix spikes and LCSs. Using a data base of 20-30 points to calculate control limits from $\pm$ 3 standard deviations from the mean. The limits should be updated yearly.

Table 5. Calibration and QC Acceptance Criteria

Parameter	Range for Q ug/L	Limit for s ug/L	Range for x ug/L	Range p (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.7	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethylbenzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	14.3-27.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in ug/L.
s = Standard deviation of four recovery measurements, in ug/L.
x = Average recovery for four recovery measurements, in ug/L.
p = Percent recovery measured.
D = Detected; result must be greater than zero.

6.6. Data Interpretation

The qualitative and quantitative analysis for the compounds in Table 1 shall be performed primarily through the use of manufacturer supplied identification-quantitation routines. The report generated should in all but the most extreme cases allow the GC-MS operator to validate the data strictly by the information supplied in the quantitation report.

6.6.1. GC-MS-DS Sample Reports. The GC-MS operator shall set up the data system as indicated by sections 6.1.1. to 6.1.3.

6.6.2. Qualitative analysis

6.6.2.1. An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with the reference mass spectrum. Reference mass spectra should be obtained on the user's GC-MS. These reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component within the Relative Retention Time (RRT) window of the analyte; and (2) correspondence of the sample component and the standard component mass spectrum by visual comparison. Care must be taken when acquiring reference spectra so as to avoid creation of reference spectrums that are contaminated with the spectrum from coeluting analytes.

6.6.2.2. The retention time window should be set to +/- 0.5 minutes in the ID file(s). To be identified analyte retention times must be within this window. This is a very large window, typically analyte retention times agree with standard retention times within a second or less.

6.6.2.3. (1) All ions present in the standard mass spectra at a relative intensity greater than 20% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% relative between the reference and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent). Visual comparison is adequate.

6.6.2.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

6.6.2.5. When requested by the client or required by the requested method, non-target compounds may be tentatively identified by library searching. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum. Ions less than 10% intensity may be removed by the GC-MS threshold routine and may not be present in the sample spectrum.

(2) Relative abundance of ions of similar mass should agree within ± 20% relative between the reference and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum, as long as they are of sufficient intensity to be detected.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum may have been inadvertently subtracted from the sample spectrum due to background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

6.6.2.6. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

6.6.2.7. It should be noted that from a mass spectrum it is frequently impossible to differentiate isomers, particularly for aliphatic hydrocarbons and aromatics. When reporting these compounds care should be taken so as to remain consistent for a particular compound appearing in different samples from a single site or contamination source. In the case of multiple hits of the same compound or isomer, a general description of the isomer may be reported several times. For example:

LIBRARY SEARCH SUMMARY VOLATILE FRACTION

SAMPLE	COMPOUND	CONCENTRATION (ug/L)
100000	Trimethyl benzene isomer	123.
	Trimethyl benzene isomer	92.
	Trimethyl benzene isomer	54.

However, if the analyst is confident that there is sufficient mass spectral uniqueness to identify to the specific isomer the specific isomer should be reported.

Table 6. ISTD/Target Analyte Reference Information

Analyte	Type	R.T. (min)	Primary Ions	Secondary Ions	
Fluorobenzene	I	10.69	96	70	50
Dichlorodifluoromethane	T	2.32	85	87	
Chloromethane	T	2.59	50	52	
Vinyl Chloride	T	2.75	62	64	
Bromomethane	T	3.27	94	96	
Chloroethane	T	3.45	64	66	
Trichlorofluoromethane	T	3.89	101	103	
1,1-Dichloroethene	T	4.84	96	61	63
Methylene Chloride	T	5.84	84	86	49
trans-1,2-Dichloroethene	T	6.42	96	61	63
1,1-Dichloroethane	T	7.27	63	65	83
2,2-Dichloropropane	T	8.44	77	79	41
cis-1,2-Dichloroethene	T	8.47	96	61	63
Chloroform	T	9.12	83	85	
Bromochloromethane	T	8.92	128	49	130
Acrolein	T	4.64	56	55	
Methyl Iodide (Iodomethane)	T	5.11	142	127	
Carbon disulfide	T	5.23	76	78	
Acetone	T	4.96	43	58	
Allyl Chloride	T	5.59	41	39	76
Acrylonitrile	T	7.48	53	52	
Chloroprene	T	7.48	53	88	51
Propionitrile	T	8.61	54	55	
Methacrylonitrile	T	8.91	41	39	67
Dibromofluoromethane	S	9.43	111	113	81
1,2-Dichloroethane	T	10.19	62	98	64
1,2-Dichloroethane-d4	S	10.04	65	102	67
Chlorobenzene-d5	I	15.10	82	117	119 54
1,1-Dichloropropene	T	9.78	110	75	77
Carbon Tetrachloride	T	9.78	117	119	82
Benzene	T	10.16	78	77	79
Trichloroethene	T	11.33	130	97	95
1,2-Dichloropropane	T	11.67	63	41	76
Bromodichloromethane	T	12.12	83	85	
Dibromomethane	T	11.85	93	95	174
Toluene	T	13.27	91	92	
1,1,2-Trichloroethane	T	13.82	97	99	
1,2-Dibromoethane	T	14.49	107	109	
Methyl Methacrylate	T	11.92	41	69	100
Toluene-d8	S	13.18	98	100	
2-Chloro Vinyl Ether	T	12.59	63	106	65
cis-1,3-Dichloropropene	T	12.79	75	77	
trans-1,3-Dichloropropene	T	13.58	75	77	
Vinyl Acetate	T	7.46	43	86	
Hexane	T	7.06	56	57	41 43
2-Butanone (MEK)	T	8.53	72	43	
1,1,1-Trichloroethane	T	9.44	97	99	
Dibromochloromethane	T	14.35	129	127	131

Table 6. Continued

Analyte	Type	R.T. (min)	Primary Ions	Secondary Ions	
Ethyl Methacrylate	T	13.72	69	41	
4-Methyl-2-pentanone (MIBK)	T	13.03	43	58	57
1,4-Dichlorobenzene-d4	I	17.98	152	150	115
1,3-Dichloropropane	T	14.04	76	78	
Tetrachloroethene	T	14.03	164	166	129
Chlorobenzene	T	15.14	112	77	114
1,1,1,2-tetrachloroethane	T	15.24	131	133	117
Ethylbenzene	T	15.28	106	91	
m&p-Xylene	T	15.44	106	91	105
o-Xylene	T	15.93	106	91	105
Styrene	T	19.07	104	78	103
Bromofluorobenzene	S	16.57	174	95	176
2-Hexanone	T	14.17	43	58	100
Isopropylbenzene	T	16.39	105	120	
1,1,2,2-Tetrachloroethane	T	16.74	83		85
1,2,3-Trichloropropane	T	16.79	110	75	61
1,2,4-Trimethylbenzene	T	17.76	105	91	
1,3-Dichlorobenzene	T	17.90	146	111	148
1,4-Dichlorobenzene	T	18.00	146	111	148
1,2-Dichlorobenzene	T	18.45	146	111	148
1,2-Dibromo-3-chloropropane	T	19.36	157	75	155
trans-1,4-Dichloro-2-butene	T	17.00	89	75	124
Pentachloroethane	T	17.52	117	167	
Bromoform	T	19.34	173	171	175
n-Propylbenzene	T	16.94	120	91	
2-Chlorotoluene	T	17.07	91	126	
4-Chlorotoluene	T	17.23	91	126	
sec-Butylbenzene	T	18.02	105	134	
tert-Butylbenzene	T	17.68	119	91	134
n-Butylbenzene	T	18.68	91	92	134
p-Isopropyltoluene	T	18.24	119	91	134
1,2,3-Trichlorobenzene	T	21.54	180	182	145
1,2,4-Trichlorobenzene	T	20.87	180	182	145
Napthalene	T	21.21	128	127	
Bromobenzene	T	16.77	77	156	158
Hexachlorobutadiene	T	21.12	225	223	227
Methyl-tert-butyl ether	T	6.45	73	57	

I = Internal Standard
T = Target Compound
S = Surrogate Spike Compound

R.T. = Retention Time. The Retention Times listed can vary by ± 5 minutes based on column and instrument conditions.

6.6.3. Quantitative Analysis

6.6.3.1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one indicated in Table 6.

6.6.3.2. The data system calculates each identified analyte.

Concentration Reported by Data System

$$\text{Concentration (ug/L)} = \frac{(Ax)(Is)}{(Ais)(RF)(Vo)}$$

Ax = Area of characteristic ion for compound being measured.
Is = Amount of internal standard injected (ng)
Ais = Area of characteristic ion for the initial standard
RF = Mean relative response factor for the compound being measured from the initial calibration.
Vo = Volume of water purged (5 mL)

The final result is calculated as follows:

Water and Water-Miscible Waste

$$\text{Concentration (ug/L)} = \frac{(C_r)(5.0\ mL)}{(V_o)}$$

C_r = Concentration Reported by data system.
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste

Medium Level:

$$\text{Concentration (ug/Kg)} = \frac{(Cr)(Vt)(5.0\ mL)}{(Vi)(Ws)(S)}$$

Low Level:

$$\text{Concentration ug/Kg)} = \frac{(Cr)(0.5\ mL)}{(Ws)(S)}$$

Where: Cr = Same as for water
Vt = Volume of total extract (uL)
Vi = Volume of extract added (uL) for purging
Ws = Wet weight of sample extracted or purged (g)
S = Fraction of solids (100 - % moisture)/100. (Ws)(S) converts sample weight to a dry weight basis.

If the use of regression curves is necessary TestAmerica will follow the requirements and use the equation from 8000B of SW-846.

6.6.3.3. An estimate of concentration for the library search compounds (if required) in the sample will be made. The formula is:

$$\text{Concentration} = \frac{(A_x)(Cis)}{(Ais)}$$

The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

6.6.3.4. Report results without correction for recovery data. When duplicates and spiked samples are analyzed report all data obtained with the sample results.

7. QUALITY CONTROL

Each Division that uses these methods is required to conform to the QAP. The laboratory must maintain records to document the quality of the data generated and these records will be regularly audited. The records must be complete and well organized. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method or those generated in-house that meet the minimum performance specifications of this method.

The experience of the analyst performing GC-MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

7.1. Method Validation Study

A Method Validation Study is required. Four LCS standards at 20 ug/L must be analyzed. The standard deviation and mean concentration values must meet the limits in Table 5. Repeat the MVS as required in section 6.2.

7.2. BFB Criteria

The GC-MS system must be tuned to meet the BFB specifications in Table 2 at the beginning of each 12 hour period. All standards, samples, blanks, and matrix spikes must be analyzed within 12 hours of BFB.

7.3. Initial Calibration Curve

A five point curve is required for each instrument. The mean relative response factor for the SPCC compounds indicated in Table 1 must be greater than 0.300 (>0.100 for bromoform). All CCCs must have mean percent RSD values of less than 30%. If the %RSD for any analyte is greater than 15%, a calibration curve must be generated using first or second order regression.

7.4. Initial Calibration Verification Standard (ICVS)

The analysis of an independent reference standard, ICVS, is required immediately following each curve. The ICVS should be quantitated using the calibration curve. If the quantitated result is not within ±30%, of the true value, it can be reanalyzed. If an acceptable ICVS can not be re-analyzed, the problem must be determined and corrected. A new initial calibration curve must be generated for the compounds that are out of control. Analytical results can not be accepted until an acceptable ICVS has been analyzed.

7.5. Continuing Calibration

A 50 ug/L continuing calibration standard must be analyzed for each 12 hour period. The SPCC compounds must have relative response factors of greater than 0.300 (>0.100 for bromoform). All CCCs must have a % Drift of less than 20%. A separate continuing calibration is required for ambient and heated samples.

7.6. Method Blanks

Method blanks are required prior to the analysis of samples in each 12 hour sequence. Method blanks must be carried through all stages of sample preparation and measurement. If internal standard and surrogate recovery limits are exceeded contact your Supervisor. For a blank to be "in control" no analytes may be present above the reporting limit. If any compound is detected above the RL in a blank, and is reported in a sample result, the data must be flagged on the sample report. The amount detected in the blank should be indicated on the report.

7.7. Internal Standards

Internal standard areas for samples and matrix spikes must be within -50 to +100% of the CCVS internal standard areas. Reanalysis is required if the internal standard limits are exceeded. If upon reanalysis the results are in control, then submit only the second set of data. If upon reanalysis the results are again out of control, submit both sets of data to your Supervisor for review. Reanalysis at a dilution is

acceptable. If acceptable internal standard areas can not be achieved it should be reported along with the sample results so that the client may determine the usability of the data.

7.8. Surrogate Recoveries

Surrogate recoveries must meet the limits in section 6.4.3.5. If the limits are exceeded reanalysis is required. If the limits are exceeded upon reanalysis submit both sets of data to your supervisor. Dilution prior to reanalysis is permitted if a matrix effect is suspected. If acceptable surrogate recoveries can not be achieved it should be reported along with the sample results so that the client may determine the usability of the data.

7.9. Matrix Spikes/Matrix Spike Duplicates

If matrix spike recovery limits in Table 5 are exceeded, the analysis of a LCS is required. MS/MSD analysis is required per batch of 20 samples or less of similar matrix.

7.9.1 The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked sample}) - (\text{Unspiked sample})}{\text{True Value}} \times (100)$$

7.9.2. The calculation for Precision as Relative Percent Difference (RPD) is:

$$\text{RPD} = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{(\text{Sum of the Values}) / 2}$$

Precision (RPD) should be less than 20%. If the precision is greater than 20% the spike amount and sample results should be evaluated. If the spike amount is appropriate for the sample result, then the MS/MSD should be repeated to confirm sample inhomogeneity. MS/MSD results that are not within the control limits must be appropriately flagged.

7.10. Laboratory Check Standard

LCS evaluation is required when the matrix spike or matrix spike duplicate results exceed the recovery limits in Table 5. If the LCS analysis results are within the limits for the analyte(s) of concern, the sample results are reportable. If the LCS analysis results are outside of the limits for the analyte(s) of concern, sample results for that analyte can not be reported. A problem exists with the analytical system and a Corrective Action Report is required. After the successful analysis of an LCS, the samples and MS/MSD may be reanalyzed.

7.11. Retention Time Requirements

Retention time windows for compound identification should be set at I 0.5 minutes. If it appears that the retention time has

shifted by more than 0.5 minutes, then a quality control standard should be analyzed. If the retention time has shifted by more than 0.5 minutes then recalibration is required. If the retention time shift is sample specific, then the sample should be diluted and repeated to correct the problem. The sample results must be flagged in the retention times can not be met.

7.12. In-house Control Limits

In-house control limits will be developed for LCSs, matrix spikes, and surrogates using statistical process control techniques. These control limits must meet or exceed the specifications in this SOP.

7.13. Method Detection Limit Studies

Method Detection Limit Studies are required per the MDL SOP and when significant changes in the analytical method are made. Analysts should consult their supervisor about whether or not a change warrants a MDL Study. Consider performing a MDL study whenever MVS analysis is required (6.2.). At a minimum an MDL study will be analyzed annually.

8. REFERENCES

1. USEPA SW-846, "Method 8260A: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique", Office of Solid Waste, Revision 1, September 1994.

2. "Definition and Procedure for the Determination of the Method Detection Limit", Revision 1.11, Appendix B, 40 CFR 136.

VAP APPENDIX

The following modifications to this SOP will be applied to samples received in support of the Voluntary Action Program (VAP).

I. When a first or second order regression curve is required for compounds exceeding 15% RSD in the initial calibration, the correlation coefficient of the curve must be at least 0.990 or recalibration is required. When using regression conversion VAP samples TestAmerica will follow the requirements outlined in 8000 B of SW-846.

II. Samples that require n-Hexane will be analyzed using the same quality control criteria as outlined in this SOP. LCS/MS/MSD control limits will be statistically generated yearly. Please see sections 6.5.7, 7.9 and 7.10 for use and corrective action of these quality control indicators. Concentration of calibration standards for n-Hexane are double the concentrations listed in Table 3.